GLOBAL JOURNAL OF ENGINEERING SCIENCE AND RESEARCHES

THERMODYNAMIC STUDIES OF ANIONIC SURFACTANT SODIUM DODECYL SULPHATE (SDS) IN AQUEOUS AND MIXED SOLVENTS(1-PROPANOL AND ISO-PROPANOL) SYSTEM

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ABSTRACT

The micellization behavior of anionic surfactant SDS in water and with 1-propanol and iso-propanol solvents media have been investigated by conductometric method, conductance were monitored conductometrically using digital conductometer. The obtained results have been used to estimate the thermodynamic parameters of micellization. Experimental data indicate that the CMC of surfactant increases with temperature, ΔG^0 is negative and remains practically constant indicating that the micellization process is exothermic in nature ΔH^0 is also negative and decrease with the temperature, indicating that the formation of micelles becomes increasingly exothermic as the temperature increased. The ΔS^0 was positive in all temperature range, decreases with increase in temperature, indicating that the micellization process is endothermic.

Keywords: *micellization, conductometric, thermodynamic, endothermic, exothermic*

I. INTRODUCTION

Anionic surfactants like sodium dodecyl sulphate (SDS), possess valuable characteristics like emulsification, wetting, water proofing, repellence, spreading, micelliation, etc. which are relevant in several applications such as pharmaceuticals, enhanced oil recovery , metallurgical process for ore concentration, and solubilization of water insoluble dyes. Investigations about the micellization characteristics of different types of surfactants are often carried out mostly in water and in aqueous media containing additives that can alter the water structure. The importance of studying micellization of surfactants in water-organic mixed-solvent systems is driven by both fundamental and practical considerations since the interfacial phenomena and application of surfactants in many industrial processes largely depend on it.[1-5] The formation of micelles is generally understood in the terms of hydrophobic effect, which is the main driving force behind the formation of micelles in the solution.[6-7] Addition of small amount of organic solvent has been known to developed marked changes in the critical micelle concentration (CMC) of the ionic surfactants due to the tendency of the added organic solvent either to break or make the water structure through the solvation of the hydrophobic tail of the surfactant by the hydrocarbon (hydrophobic) part of the organic solvent. In the addition to the criterion of the solvent's ability to form hydrogen bond, changes in the polarity or the hydrophobicity of the solvent media are also expected to play a critical role in determining the micellar behavior of ionic surfactants.[8] Studies on the micellar behavior of the ionic surfactants in aqueous and mixed aqueous organic-solvent media, therefore, assume significance in the understanding the micellization process.

In this research, we have reported the result of the conductometric studies on the micellar behavior of the anionic surfactant, sodium dodecyl sulphate (SDS) in aqueous and mixed aqueous-organic (1-propanol and iso-propanol) solvent media at **298.15[0]K, 303.15[0]K, 308.15[0]K and 313.15[0]K**.

II.MATERIAL AND METHODS

Sodium dodecylsulphate (SDS), from BDH was recrystallized several times from hot ethanol and dried under vacuum. 1-Propanol and iso- Propanol (BDH, AR) were purified by drying over calcium oxide for several days and then refluxing with fresh calcium oxide for four hours and distilled. The distilled 1-PrOH & iso -PrOH was then shaken

with anhydrous calcium chloride and kept for 24 hours. Finally the propanol was redistilled after decantation and middle fraction of the alcohol was collected.

Conductometric measurement
The specific conductivity for the surfactant solutions were measured as a function of anionic surfactant concentration with a Digital conductivity Analizer [ANALABS, model:µ con cal5] at 1 KHz. The pyrex conductivity cell of cell constant 0.985 cm-1 was used having the bright platinum discs electrodes, containing about 200ml of solution. The conductivity cell with a sample was immersed in the thermostat water both with the temperature fluctuation within ±0.010K. The conductivity cell was calibrated with standard decinormal aqueous KCl solution. The precision of the measurements was within ±0.003 m S cm-1.The cell was cleaned with chromic acid and finally washed with conductivity water before each run. A range of concentrations of the surfactants in each case was produced by adding well cooled stock solutions of appropriate concentration from a weight burette to a known quantity of the solvent mixture in the conductivity cell. In the present investigation the specific conductance data have been measured at different temperature (298.15, 303.15, 308.15 and 313.15 K).

III.   RESULTS AND DISCUSSION

The specific conductivity of the dilute solutions of anionic surfactant SDS in water, 1-propanol + H_2O and iso-propanol + H_2O mixtures at different mass fractions have been measured as a function of the concentration C, at different temperature. The values of the specific conductance versus SDS concentration for the studied systems have been plotted in Figures - (1.10, 1.11-1.14 and 1.21-1.24). The values of critical micelle concentration (CMC) of SDS, α and thermodynamic parameters obtained from these plots are given in **Table- 1.1 and 1.2** respectively for different co- solvent compositions and temperature.
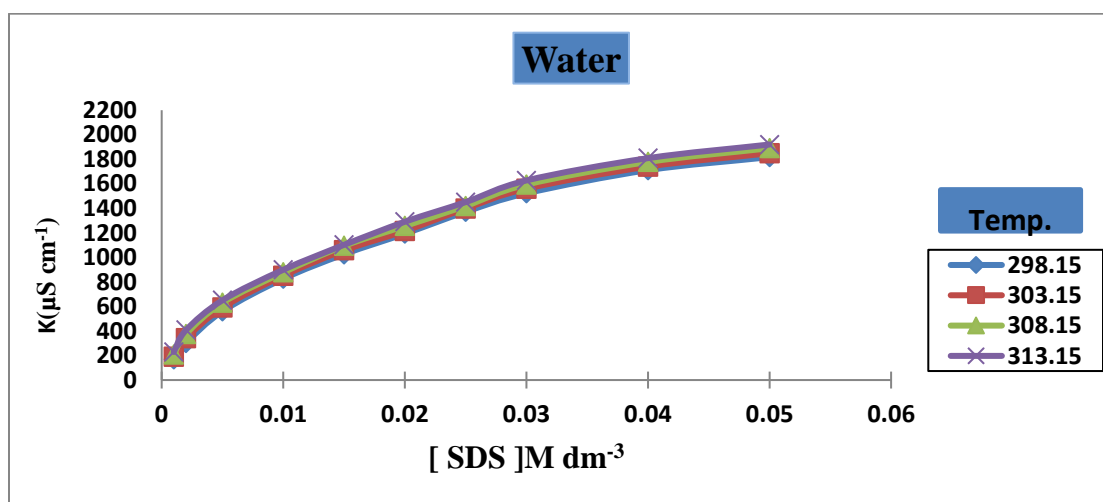

Fig : I A (1.10) Plots of Ϗ Vs M for SDS in Water at different temperatures

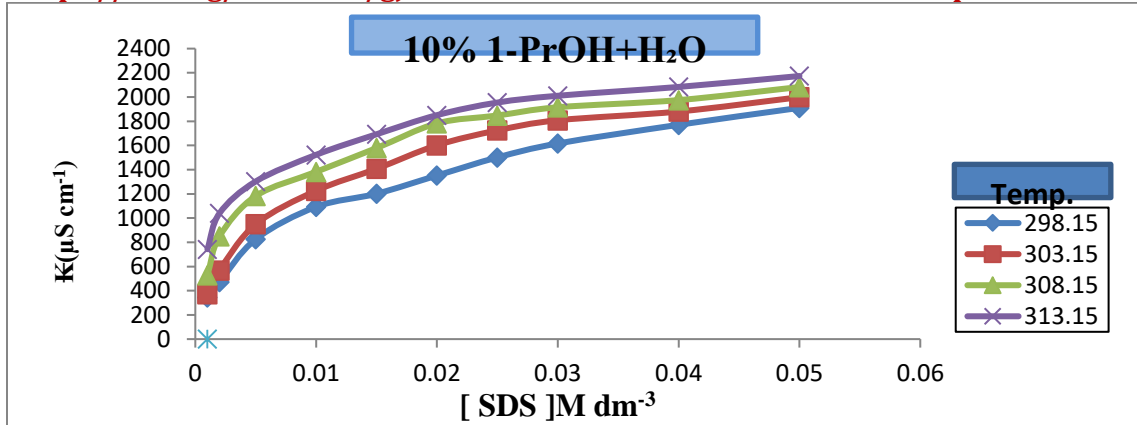*Fig : I A (1.11) Plots of 𝒦 Vs M for SDS in 10% 1- PrOH+Water at different temperatures*

Fig : I A (1.12) Plots of 𝒦 Vs M for SDS in 20% 1- PrOH+Water at different temperatures
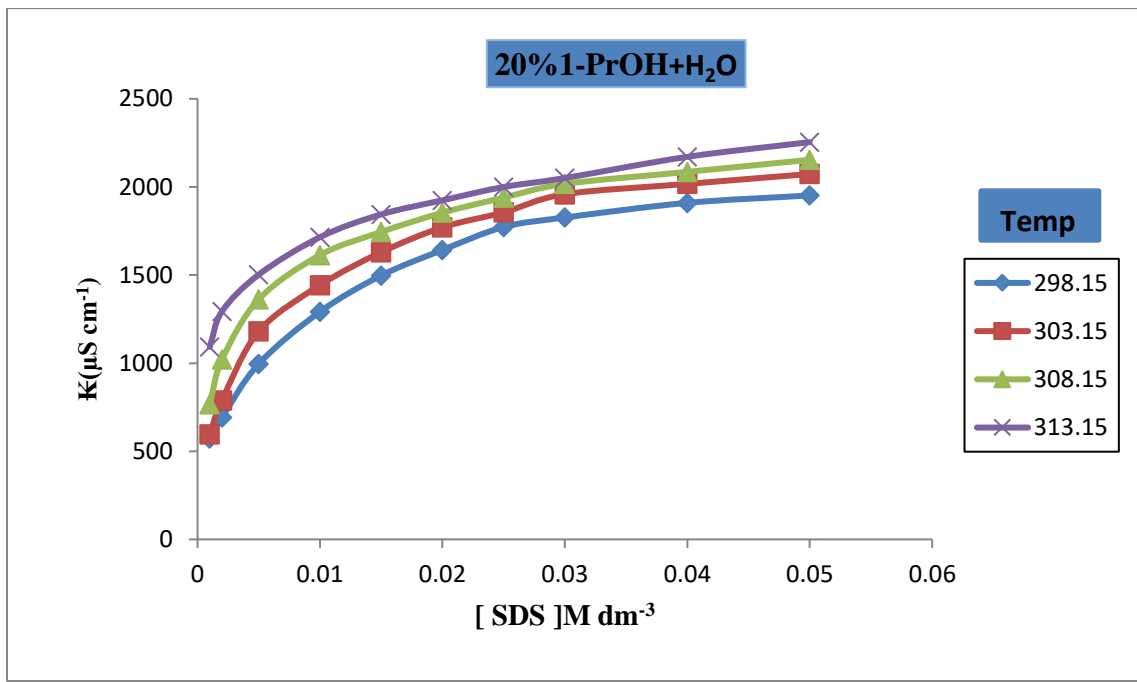
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Fig : I A (1.13) Plots of 𝒦 Vs M for SDS in 30% 1- PrOH+Water at different temperatures

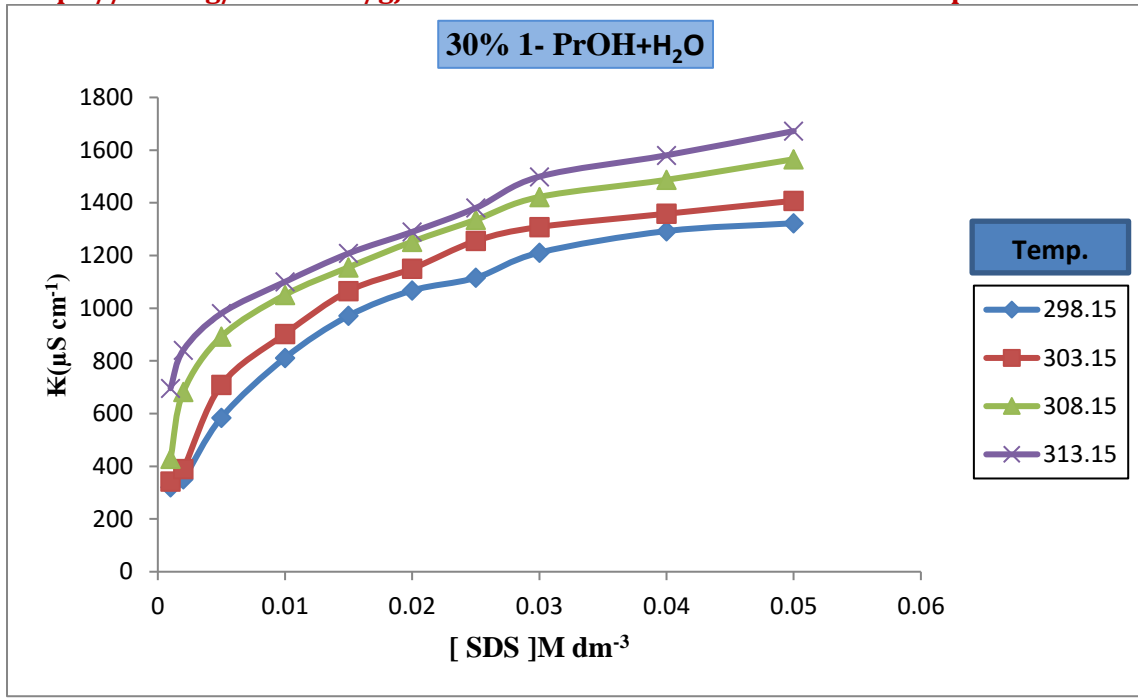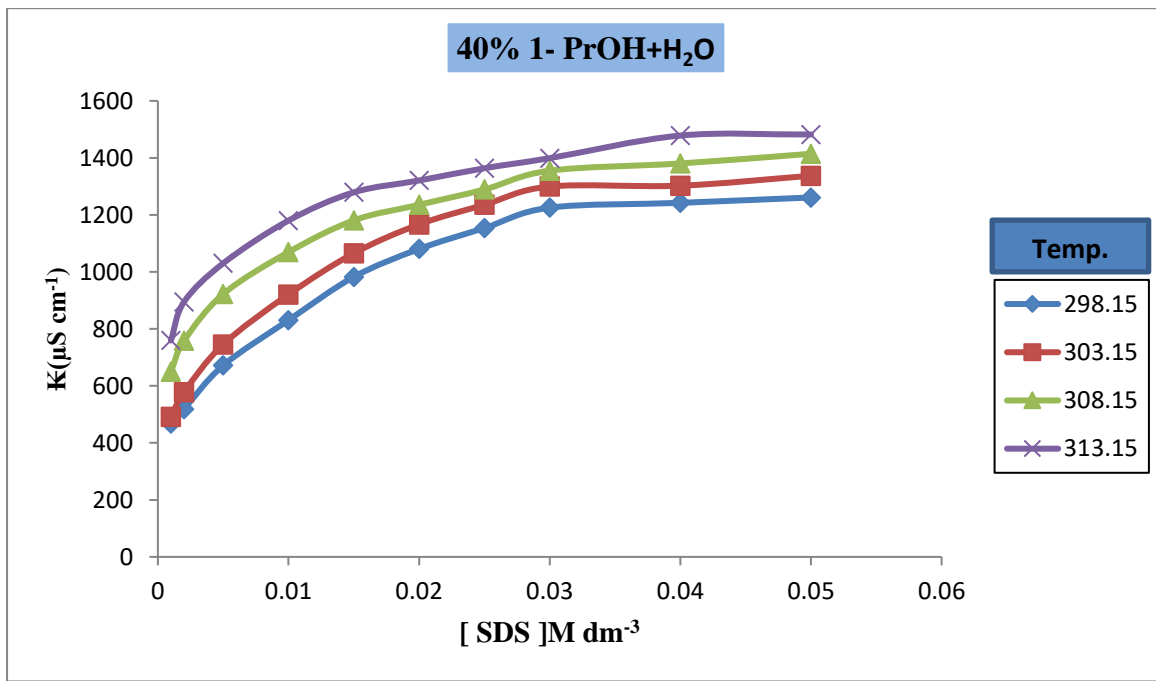*Fig : I A (1.14) Plots of 𝒦 Vs M for SDS in 40% 1- PrOH +Water at different temperatures*

TABLE-(1.1) : Values of The Critical Micelle Concentration (CMC), The Degree of Counter-ion Association (α) and The Thermodynamic Parameters of Micellization for SDS in Water and 1-PrOH + H₂O Mixtures at Different Temperatures

| T (^0K)	CMC (mol dm^{-3})	α	$-\Delta G^0_{mic}$ (kJmol^{-1})	$-\Delta H^0_{mic}$ (kJmol^{-1})	ΔS^0_{mic} (Jk^{-1}mol^{-1})	ΔG^0_{trans} (kJmol^{-1})	$\Delta C_p^0_{mic}$ (Jk^{-1}mol^{-1})
			H₂O				
298.15	0.027	0.767	10.98	3.96	32.87		
303.15	0.028	0.766	11.1	4.09	32.53		-16.18
308.15	0.029	0.765	11.14	4.23	31.39		
313.15	0.03	0.765	11.25	4.37	31.56		
			10% 1-PrOH +H₂O				
298.15	0.015	0.47	15.9	5.64	47.69	-4.92	
303.15	0.019	0.48	15.96	5.84	46.81	-4.86	-23.52
308.15	0.022	0.5	16.11	6.03	46.25	-4.97	
313.15	0.025	0.55	16.43	6.23	46.22	-5.18	
			20% 1-PrOH +H₂O				
298.15	0.026	0.44	14.07	4.99	42.21	-3.09	
303.15	0.026	0.46	14.12	5.16	41.42	-3.2	-20.28
308.15	0.029	0.46	14.17	5.33	40.66	-3.03	
313.15	0.031	0.47	14.21	5.51	39.87	-2.96	
			30% 1-PrOH +H₂O				
298.15	0.027	0.63	12.28	4.41	36.78	-1.3	
303.15	0.029	0.64	12.48	4.56	36.61	-1.38	-18.55
308.15	0.03	0.66	12.66	4.71	36.38	-1.52	
313.15	0.032	0.68	12.83	4.86	36.12	-1.58	
			40% 1-PrOH +H₂O				
298.15	0.029	0.67	11.62	4.16	34.82	-0.64	
303.15	0.031	0.69	11.7	4.31	34.29	-0.6	-16.78
308.15	0.033	0.7	12.12	4.45	34.89	-0.98	
313.15	0.034	0.71	12.31	4.59	34.73	-1.06	
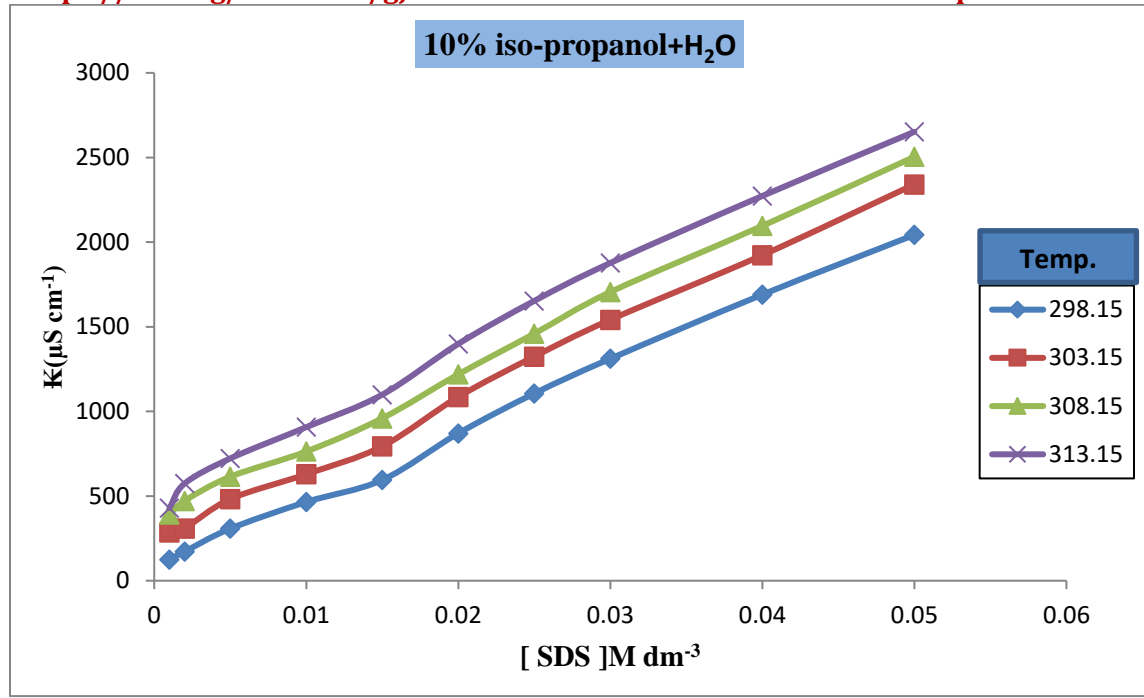
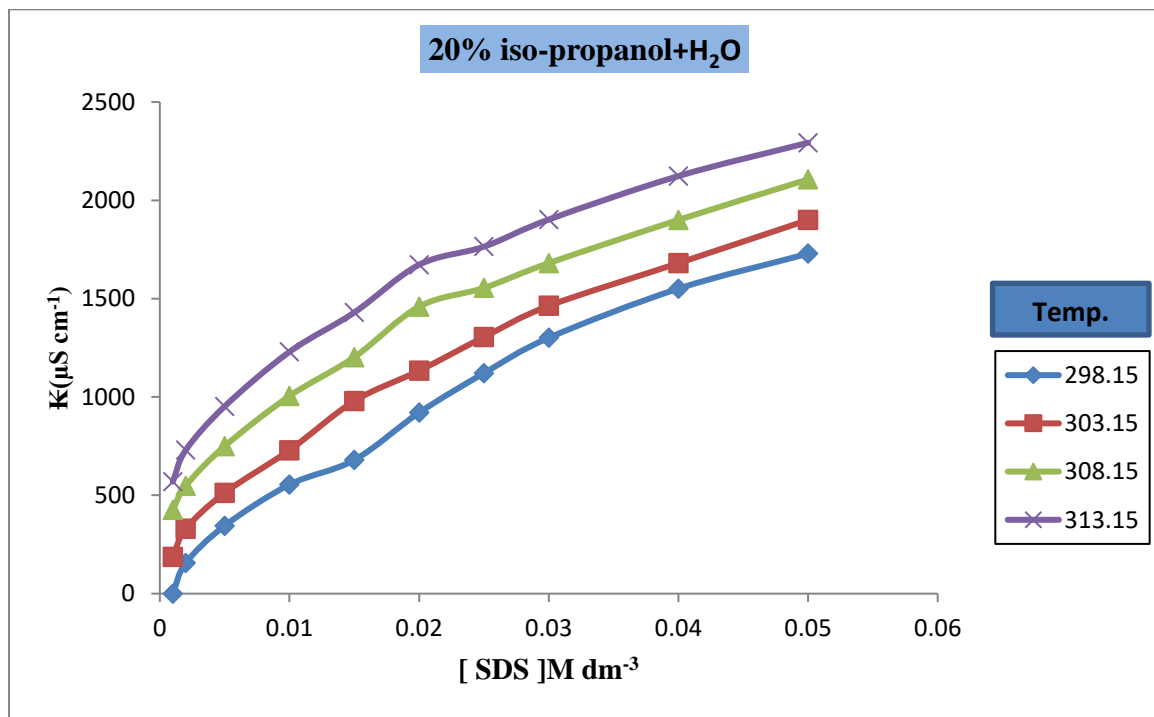*Fig : I A (1.21) Plots of $\mathcal{K}$ Vs M for SDS in 10% Iso-propanol+Water at different temperatures*

Fig : I A (1.22) Plots of $\mathcal{K}$ Vs M for SDS in 20% iso-propanol+Water at different temperatures
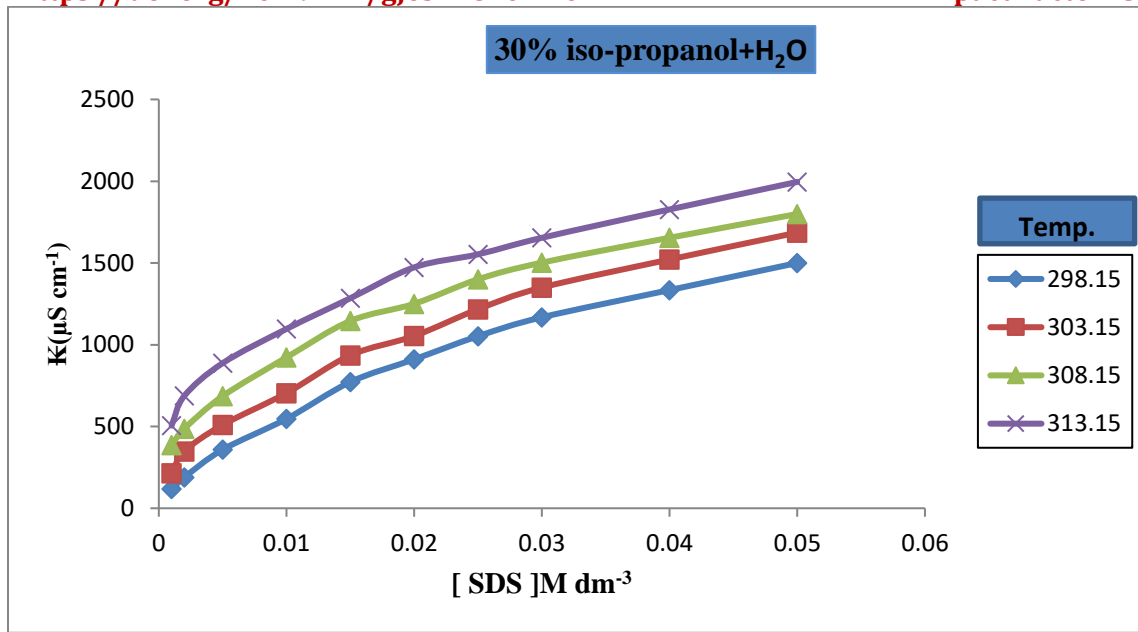
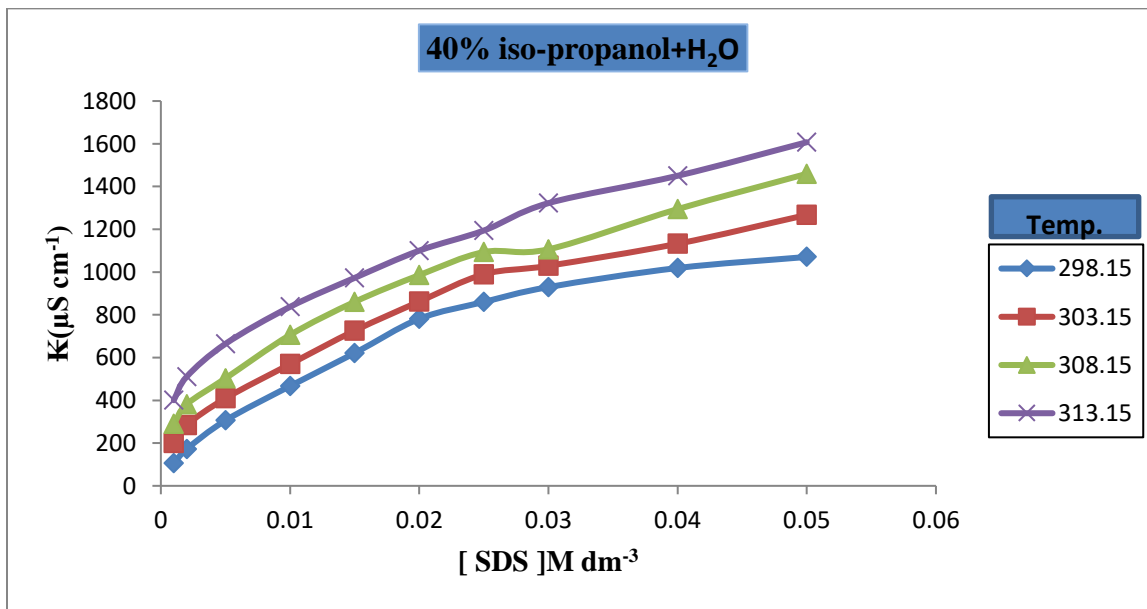*Fig : I A (1.23) Plots of 𝒦 Vs M for SDS in 30% iso-propanol+Water at different temperatures*

Fig : I A (1.24) Plots of 𝒦 Vs M for SDS in 40% iso-propanol+Water at different temperatures

TABLE- (1.2) : Values of Critical Micelle Concentration (CMC), Degree of Counter-ion Association (α) and Thermodynamic Parameters of Micellization for SDS in iso-propanol + H₂O Mixtures at Different Temperatures.

T (^{0}K)	CMC (mol dm^{-3})	α	- ΔG^0_{mic} (kJmol^{-1})	- ΔH^0_{mic} (kJmol^{-1})	ΔS^0_{mic} (JK^{-1}mol^{-1})	ΔG^0_{trans} (kJmol^{-1})	$\Delta C_p^0{}_{mic}$ (JK^{-1}mol^{-1})
			10% iso-propanol +H₂O				
298.15	0.015	0.39	16.73	6.00	50.12	-5.75	

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303.15	0.016	0.41	16.81	6.21	49.25	-5.71	-25
308.15	0.018	0.42	16.97	6.41	48.67	-5.83	
313.15	0.019	0.43	17.23	6.62	48.41	-5.98	
			20% iso-propanol +H₂O				
298.15	0.016	0.41	16.25	5.78	48.73	-5.27	
303.15	0.017	0.43	16.32	6.00	47.84	-5.22	-23.61
308.15	0.019	0.44	16.57	6.18	47.6	-5.43	
313.15	0.021	0.45	16.83	6.38	47.37	-5.58	
			30% iso-propanol +H₂O				
298.15	0.018	0.42	15.79	5.68	47.28	-4.81	
303.15	0.019	0.43	15.86	5.87	46.45	-4.76	-23.14
308.15	0.021	0.46	15.91	6.06	45.58	-4.77	
313.15	0.023	0.47	16.24	6.26	45.61	-4.99	
			40% iso-propanol +H₂O				
298.15	0.02	0.44	15.14	5.7	45.08	-4.16	
303.15	0.024	0.45	15.48	5.89	45.18	-4.38	-23.49
308.15	0.025	0.47	15.89	6.09	45.48	-4.75	
313.15	0.027	0.48	18.23	6.29	51.93	-6.98	

The surfactant concentration at which the micellization start is evident from the change in the slope of plots and that particular concentration is the CMC under the experimental condition. The values of CMC and α for the studied systems are also given in Table 1 and 2 for SDS with water, 1-propanol+H₂O and iso-propanol+H₂O respectively. The thermodynamic parameters were calculated from the following relations.

$$\alpha = (1 - \beta) \qquad \ldots\ldots\ldots\ldots\ldots(1)$$
$$\Delta G^0 mic = 2.303\ RT\ (2-\alpha)\ \log CMC \qquad \ldots\ldots\ldots\ldots (2)$$
$$\Delta S^0{}_{mic} = \left[-\frac{d\left(\Delta G^0_{mic}\right)}{dT} \right]_p \qquad \ldots\ldots\ldots\ldots(5)$$

$$\Delta H^0{}_{mic} = -T^2 \left[\frac{\partial\ d\left(\Delta G^0_{mic}\right)}{\partial dT} \right]_p \qquad \ldots\ldots\ldots\ldots (6)$$

Further, the Gibbs free energy of transfer values (ΔG⁰trans) which can be accounted for the effect of co-solvent on the micellization process was estimated through the relation.

ΔG⁰trans= ΔG⁰mic (w+cos) - ΔG⁰mic(w)   …..…… (7)

Where, $\Delta G^0 mic(w)$ and $\Delta G0mic\ (w+cos)$ stands for standard Gibbs free energy of the micellization in water and water+ cosolvent mixed media respectively. The change in the molar heat capacity for micelle formation $\Delta Cp^0 mic$ can be obtained from the slops of the plot of $\Delta H^0 mic$ versus temperature

$$\mathbf{\Delta Cp^0{}_{mic} = \left[\frac{\partial d\left(\Delta H^0_{mic}\right)}{d\partial T} \right]_p} \quad \ldots\ldots\ldots (8)$$

The CMC of the anionic surfactant SDS were evaluated from the inflection point in the plots of conductance against concentration of SDS. It is found that the CMC of SDS increases on increasing the temperature for a given organic solvent system. In the case of aqua-organic solvents system the CMC gradually increases with the increasing the amount of the cosolvents and the temperature of the organic substances chosen for this study . In the present work the CMC value of SDS in pure aqueous solution appear to be in good agreement. On mixing 1-PrOH and isopropanol to be an aqueous surfactant solution, an increase in CMC irrespective of the nature of the surfactant as reported in Table1.1 and 1.2. The decrease of dielectric constant of medium appears the micellization by increasing mutual repulsion of ionic heads in the micelle, hence increasing the CMC. Increase in the CMC on mixing isopropanol of the surfactant solution being more significant compared to 1-PrOH is due to lower dielectric constant of the former.

Generally, the CMC increases when co solvent (i) is water structure breaker, (ii) undergoes partial micelle penetration and (iii) lowers the dielectric constant of the medium. In the case of 1-PrOH+H_2O partial micelle penetration is possible and it also lowers the dielectric constant of the medium. Hence, 1-PrOH is the micellar structure breaker and due to lower dielectric constant than isopropanol+H_2O system. Therefore, the value of CMC is more significant in isopropanol+H_2O system than that of the 1-PrOH+H_2O system.

The formation of micelles were always found to be connected with a large, negative change in $\Delta G°$ i.e. the aggregation process is the thermodynamically favoured and spontaneous. The $\Delta G°$ value become the more negative with increase in temperature and become less negative with the increase in the co-solvent content in the mixed media. The results also show that the $\Delta H°$ values calculated for aqueous and all solvents medium are negative. The values of ΔH^0 were negative and decrease with the increase in temperature indicating that the micellization process increasingly exothermic for the ionic surfactant, SDS. As well as, on adding cosolvents into the surfactant solution, there is decrease in enthalpy change ΔH^0 irrespective of their chemical nature, again due to their intermolecular hydrogen bonding with water. The negative enthalpy value can be taken as evidence that London dispersion interaction represent the major attractive force for micellization. The overall micellization process was found to be exothermic. The entropy $\Delta S°$ values for surfactant solvent systems were positive indicating that the micellization process is entropy dominated. The standard entropy of micellization ΔS^0 was positive in all temperature range, decreases with increase in temperature, indicating that the micellizatin process is endothermic. The positive values of entropy $\Delta S°$ clearly indicate that the micellization of the studied surfactant in aqueous as well as in various solvents is governed mainly by hydrophobic interaction between the surfactants anions resulting in the breakdown of the structured water surrounding the hydrophobic groups. The heat capacity at constant pressure ΔCp^0 was determined from the slopes of eq. (8). All the values of ΔCp^0 are negative and this favours the formation of micelles is an exothermic process.   The positive values of ΔG^0trans indicates that it's responsible for the delay in the micellization of surfactants in the mixed media and their value depends on the transfer Gibbs free energies from pure water and the cosolvents in addition to their mutual interaction. As the addition of organic solvent modifies the bulk phase making it more favorable than pure water for dispersion of surfactant molecules, and transfer of hydrophobic tail from the bulk phase to the micellar region becomes less favorable, and hence ΔG^0mic values becomes less negative.

IV.   CONCLUSION

The micellization and thermodynamic behaviour of anionic surfactant, sodium dodecyl sulphate SDS in water, 1-propanol+ H_2O and iso-propanol solvent mixtures has been investigated by conductometric measurement at temperature range 298.15 to 313.15K^0. The values of CMC and degree of counter-ion association constant (α) increases with increase in the amount of organic solvent. It also indicates that the thermodynamic parameter for micellization is also thermodynamically favoured and spontaneous.

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